

REGIONAL AND EVALUATIVE LEVEL III FUGACITY MODELS
DESCRIBING THE MULTIMEDIA ENVIRONMENTAL PARTITIONING,
REACTION. AND TRANSPORT OF ORGANIC CHEMICALS

D. MACKAY
S. PATERSON

INSTITUTE FOR ENVIRONMENTAL STUDIES
UNIVERSITY OF TORONTO
TORONTO. ONTARIO CANADA M5S 1A4

REPORT TO THE ONTARIO MINISTRY OF THE ENVIRONMENT

PROJECT NO. 194 PL

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ABSTRACT

A multimedia model is developed and applied to selected organic chemicals in evaluative and real environments. The model employs the fugacity concept and treats four bulk phases: air, water, soil, and bottom sediment, which consist of subcompartments of varying proportions of air, water, and mineral and organic matter. Chemical equilibrium is assumed to apply within (but not between) each bulk phase. Expressions are included for emissions, advective flows, degrading reactions, and inter-phase transport by diffusive and non-diffusive processes. The solution of the steady-state, constant emission condition is a relatively simple algebraic expression. Input to the model consists of a description of the environment, the physical-chemical and reaction properties of the chemical, and the emission rate. The model is applied to six chemicals in the region of Southern Ontario and the calculated concentrations compared with observations. The results suggest that the model may be used to predict the likely environmental fate of chemicals and estimate concentrations for defined locations and at defined times within an order of magnitude.

Sommaire

On élabore un modèle portant sur plusieurs phénomènes pour l'appliquer à certaines substances organiques en milieux expérimental et réel. Ce modèle fait appel au concept de la fugacité et porte sur quatre phases globales de la matière : l'air, l'eau, le sol et les sédiments. Chacune de ces phases est composée de sous-catégories selon sa teneur en air, en eau, et en substances minérales et en matières organiques. On présume l'existence d'un équilibre chimique à l'intérieur de chacune des phases globales, mais non entre celles-ci. Le modèle comprend des formules pour les émanations, l'advection, les effets de dégradation et le transfert de masse par diffusion et par d'autres procédés. La solution pour les émanations en régime constant est présentée sous forme d'expression algébrique relativement simple. Le modèle fait l'analyse des données sur l'environnement, sur les propriétés physiques et chimiques de la substance et sur le débit d'émission. On applique le modèle à six composés chimiques que l'on retrouve dans le sud de l'Ontario pour ensuite comparer les résultats obtenus aux concentrations observées. Les résultats semblent indiquer que le modèle permet de prévoir le sort probable des substances chimiques dans l'environnement et d'estimer, selon un ordre de grandeur, leur concentration à des endroits et à des moments précis.

INTRODUCTION

Environmental models of varying degrees of sophistication have been developed to describe or predict the multimedia fate and behavior of organic contaminants (1,2,3,4). These models may be steady- or unsteady-state in nature and employ the chemical's physical chemical properties, reactivity, transport characteristics, and extent of release to the environment to produce a comprehensive picture of the chemical's pathways between, and ultimate concentrations in, various media, such as soil, air, water, and sediment. This modelling capability is a necessary adjunct to toxicity testing in assessing risk from chemical exposure and for determining priorities for research and regulatory action. It can be applied to new and existing chemicals.

Of concern are chemicals that are, or will be, in frequent commercial use and therefore can be expected to be discharged constantly to the environment over a period of time. Examples are pesticides, PCB's, wood preservatives, and by-products of incineration and dry-cleaning operations.

We develop here a novel, simplified, fugacity-based model to predict this steady-state behaviour. The model treats four bulk phases: air, water, soil and sediment, which consist of subcompartments of fluid (air and/or water), particulate (aerosols, suspended particles, and organic matter) and other phases (fish). Equilibrium partitioning of chemicals is assumed to apply within each of the four bulk phases.

Expressions for environmental emissions and advection into, reaction and advection from, and diffusive and non-diffusive transfer between these bulk phases are incorporated in a set of mass balance equations as previously described (2). Reducing the number of key environmental media to four permits a simple algebraic solution. Unlike previous models, non-diffusive transfer processes, such as wet and dry atmospheric particulate deposition, rain washout, leaching to groundwater from soil, and sediment resuspension, are included.

Fugacity

In previous models, partitioning of mass between phases has been described by the equilibrium criterion of fugacity as an alternative to chemical potential. Fugacity can be considered to be the partial pressure of a chemical in a phase and is related to its concentration in that phase by the expression

$$C = fZ \quad (1)$$

where C is concentration (mol/m^3), f is fugacity (Pa) and Z is the fugacity capacity ($\text{mol}/\text{m}^3\cdot\text{Pa}$). When equilibrium exists between two phases, the chemical fugacities are equal and partitioning can be described by the ratio of their Z values, that is

$$K_{12} = C_1/C_2 = fZ_1/fZ_2 = Z_1/Z_2 \quad (2)$$

where K_{12} is the dimensionless equilibrium partition coefficient. The calculation of Z values for environmental phases has been reviewed by Mackay and Paterson (1).

Briefly, Z for air is calculated using the gas law, and Z values for other phases are calculated from it using estimated partition coefficients such as sorption partition coefficients, Henry's Law constants, and bioconcentration factors. Partitioning of a chemical between the organic phases of soil, sediment, or fish and water can be described in terms of its octanol/water partition coefficient (K_{OW}) and the fraction organic content in that phase. For soil or sediment, the partition coefficient is $0.41 K_{OW} \cdot x$ L/kg where x is the organic content of the phase (1). Fish to water partitioning is described by the relationship $0.048 K_{OW}$ (5).

Chemicals move between phases by diffusive and non-diffusive processes. Diffusive transfer rates between two phases, 1 and 2, can be described, using the fugacity equilibrium concept as

$$N = D_{12}f_1 - D_{21}f_2 \quad (3)$$

where N is the flux between the two phases (mol/h), D_{12} and D_{21} are transfer coefficients with units of mol/h.Pa, and f_1 and f_2 are the phase fugacities. The difference between f_1 and f_2 determines the direction of diffusive flux which takes place from high to low fugacity. The coefficients D_{12} and D_{21} are functions of Z values, interfacial areas and

diffusion properties in adjacent phases (2). In the case of simple, reversible diffusion, D_{12} and D_{21} are equal and

$$N = D_{12}(f_1 - f_2) \quad (4)$$

It has been shown (2) that D may be expressed as the product of kAZ where k is a mass transfer coefficient and A is the interfacial area. In some cases, there may be two diffusive resistances in series, each characterized by an individual mass transfer coefficient. D may also be expressed as BAZ/Y , where B is a diffusivity and Y is the effective diffusion path length, B/Y being equivalent to k (3).

Non-diffusive or one-way transfer processes between phases, for example, wet or dry particle deposition from the atmosphere to soil or water, or suspended sediment deposition or resuspension, can also be described by a transport parameter as

$$N = GC = GZf = Df$$

where G is volumetric flow rate (m^3/h), and D again has units of $mol/Pa.h$.

Similarly, advective out-flows in air and water can be described by a flow rate ($G m^3/h$), concentration product.

$$\text{rate of advection} = GC = GZf = D_A f$$

or

$$\text{rate of advection} = k_A V Z f = D_A f$$

where k_A is a first order rate constant equal to G/V . Advective inflow can be included as GC_B or $D_A f_B$, in which subscript B refers to the background inflow concentration.

First order reaction processes in a phase can also be described by a D value as

$$\text{rate of reaction} = k_R VC = k_R VZf = D_R f$$

where k_R is a first order rate constant (h^{-1}), V is the phase volume (m^3), and D_R again has units of mol/Pa.h .

MODEL DESCRIPTION

1. Environmental Media

Four major bulk compartments are defined each of total volume, V_i , - air, water, soil, and sediment - subscripted 1-4. These phases consist of a combination of subcompartments of pure and particle phases of volume, V_{ij} , and are defined as a volume fraction, ϕ_{ij} or V_{ij}/V_i , of the bulk phase. For example, bulk water consists of "pure" water, suspended solids, and fish; soil consists of mineral matter, organic matter, water, and air; air consists of pure air and aerosols; sediment is mineral matter, organic matter, and water.

It is assumed that equilibrium exists within each bulk phases, ie. a common fugacity applies. This implies that the times required to reach equilibrium within a bulk phase are short compared to times required to reach equilibrium between bulk phases.

This environment can be evaluative in nature as described in previous papers (3,6) or can represent an actual region. We apply the model here to i) an environment scaled to represent Southern Ontario and ii) an evaluative environment of area 1 sq km with similar phase proportions. The air height has been reduced to 2000 m from 6000 m to reflect conditions of atmospheric accessibility in Southern Ontario. The compartment volumes for the two scenarios are given in Table 1.

Table 1

Properties of the Phases: Volume Fractions, Organic Carbon (OC) Fractions, Densities (kg/m^3), Volumes, (m^3), Areas (m^2), and Depths (m)

Bulk Phase (i)	Subcompartments (j) Volume Fractions				Fraction OC in solids	Density	Volumes		Areas		Depths
	Air (1)	Water (2)	Solids (3)	Biota (4)			S. Ontario	Evaluative	S. Ontario	Evaluative	
Air (1)	1.0	0	5×10^{-12}	0	--	1.19	4×10^{14}	2×10^9	2×10^{11}	1×10^6	2×10^3
Water (2)	0	1.0	5×10^{-6}	1×10^{-6}	0.2	1000	4×10^{12}	2×10^7	8×10^{10}	4×10^5	50
Soil (3)	0.2	0.3	0.5	0	0.02	1500	1.2×10^{10}	6×10^4	12×10^{10}	6×10^5	0.1
Sediment (4)	0	0.7	0.3	0	0.04	1420	8×10^8	4000	8×10^{10}	4×10^5	0.01
Density	1.19	1000	2400	1000							

Fugacity Capacities

For each subcompartment, a Z value or fugacity capacity is calculated. These values are then combined with the volume fractions to give an overall Z value for the bulk phase as illustrated in Table 2, ie. Z_1 is the sum of the $\phi_{1j}Z_{1j}$ terms.

1) Bulk Air

Vapor and particulate matter (aerosols) are assumed to be the principal components of the bulk air phase. From the gas law, the fugacity capacity for vapour or pure air, Z_{11} , is calculated as $1/RT$ where R is the gas constant ($8.314 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$) and T is the absolute temperature. Particles in air occupy a volume fraction, ϕ_{13} of 2×10^{-11} , equivalent to about $50 \text{ ug}/\text{m}^3$. Partitioning between particulate and gaseous air phases is inversely proportional to the vapor pressure (7) with the particulate-air partition coefficient expressed as

$$K_{13} = 6 \times 10^6 / P_L^S = Z_{13} / Z_{11}$$

where P_L^S is the sub-cooled liquid vapor pressure (Pa). Therefore the fugacity capacity for particulates in air is given by

$$Z_{13} = 6 \times 10^6 \cdot Z_{11} / P_L^S$$

and the overall Z value is calculated as shown in Table 2.

ii) Bulk Water

Water is considered to consist of a pure water phase containing suspended sediment particles and fish. The fugacity capacity for pure water Z_{22} is defined as the reciprocal of the Henry's Law constant or $1/H$ (1). The Z values for the particle (Z_{23}) and biota or fish (Z_{24}) phases are calculated as $PK_{1j} \cdot \rho_{1j} \cdot Z_{22}$ (or $K_{1j} \cdot Z_{22}$) where PK_{1j} is the particle (fish)/water partition coefficient (L/kg), K_{1j} is the dimensionless partition coefficient, and ρ_{1j} is density of the particulate or fish phases (kg/L) (1). In the calculation of PK_{23} a value of 0.2 is assumed for mass fraction organic content (x_{1j}). The fish/water partition coefficient, PK_{24} , is $0.048 K_{OW}$. These Z values are combined with their appropriate volume fractions, ϕ_{23} and ϕ_{24} of 5×10^{-6} (equivalent to about 12 mg/L) and 10^{-6} , respectively, to give an overall fugacity capacity as shown in Table 2. It should be noted that the concentration of "fish" is unrealistically high and represents the inclusion of other biota, especially micro-organisms.

iii) Bulk Soil

Following Jury et al (8), soil is assumed to contain a soil particle phase (volume fraction ϕ_{33} of 0.5) combined with air (ϕ_{31} of 0.2) and water (ϕ_{32} of 0.3). The fugacity capacity for the solid phase, Z_{33} , is calculated as described earlier from the product of the pure soil/water partition coefficient and the Z value for water as $K_{32} \cdot Z_{22}$. The fraction organic content in the solid phase x_{33} is 0.02, and the density ρ_{33} is 2.4 kg/L. The Z values of soil, air, and water are combined, as shown in Table 2, with their volume fractions to give an overall fugacity capacity.

Table 2
Definition of Z values

Subcompartments (j)	Z_{ij}	Reference
Air (i_1)	$1/RT$ $R = 8.314 (\text{Pa m}^3/\text{mol K})$ $T = \text{absolute temp K}$	(1)
Water (i_2)	$1/H$ or C^S/P^S $H = \text{Henry's Law constant } (\text{Pa m}^3/\text{mol})$ $C^S = \text{aqueous solubility } (\text{mol/m}^3)$ $P^S = \text{vapor pressure } (\text{Pa})$	(1)
Soil, Sediment Solids, & Water Particles (i_3)	$x_{ij}K_{OC}$ $x_{ij} = \text{fraction organic carbon}$ $K_{OC} = \text{organic carbon partition coefficient}$ $= 0.41 K_{OW}$ $\rho_{ij} = \text{density } (\text{kg/L})$	(5)
Aerosols (i_3)	$6 \times 10^6 / P_L^S RT$	(7)
Biota (fish) (i_4)	$0.048 \rho_{i4} K_{OW} / H$ $K_{OW} = \text{octanol water partition coefficient}$	(6)
Bulk Phases (i)		
Air (1)	$Z_1 = Z_{11} + \phi_{13} Z_{13}$	
Water (2)	$Z_2 = Z_{22} + \phi_{23} Z_{23} + \phi_{24} Z_{24}$	
Soil (3)	$Z_3 = \phi_{31} Z_{11} + \phi_{32} Z_{22} + \phi_{33} Z_{33}$	
Sediment (4)	$Z_4 = \phi_{42} Z_{22} + \phi_{43} Z_{43}$	

iv) Bulk Sediment

The bulk phase is assumed to consist of two subcompartments, pure sediment and sediment pore water with volume fractions of ϕ_{43} and ϕ_{42} , with values of 0.3 and 0.7, respectively. As in the case of soil, the Z value for pure sediment (Z_{43}) is calculated as $K_{42} \cdot Z_{22}$, where $x_{43} = 0.04$ and $\rho_{43} = 2.4$ kg/L, and the combined bulk Z value is deduced as in Table 2.

Transfer Parameters

Assumed transfer parameters necessary for calculation of intermedia fluxes are given in Table 3, areas being given in Table 1. These parameters are converted into D values as shown in Table 4. A summary of their derivations follows.

i) Air-Water

Chemicals move between air and water by diffusive and non-diffusive processes. Diffusive processes of volatilization and absorption are described by the parameter D_V where

$$1/D_V = 1/D_{VA} + 1/D_{VW} = 1/(k_{VA}A_{12}Z_{11}) + 1/(k_{VW}A_{12}Z_{22})$$

where k_{VA} and k_{VW} are air- and water-side MTC (mass transfer coefficients) (m/h), D_{VA} and D_{VW} the transfer parameters (mol/h.Pa), and A_{12} is the interfacial area (m^2). The reciprocals of these D terms can be considered resistances which are in series and combine to give an overall air-water transfer resistance $1/D_V$. The same mass transfer coefficients are assumed to apply to all chemicals with values of 3 m/h and 0.03 m/h for k_{VA} and k_{VW} , respectively. These values are slightly reduced from those used

Table 3

Assumed Transport Parameters

Parameter	Symbol	Value
Air side MTC over water	k_{VA}	1 m/h
Water side MTC	k_{VW}	.01 m/h
Transfer rate to higher altitude	U_S	.01 m/h (90 m/y)
Rain rate ($m^3_{rain}/m^2_{area}.h$)	U_Q	9.7×10^{-5} m/h (.85m/y)
Scavenging ratio	Q	200,000
Dry deposition velocity	U_P	10.8 m/h (.003 m/s)
Air side MTC over soil	k_{SA}	1 m/h
Diffusion path length in soil	Y_3	.05 m
Molecular diffusivity in air	B_{MA}	.04 m^2/h
Molecular diffusivity in water	B_{MW}	4.0×10^{-6} m^2/h
Water runoff rate from soil	U_{WW}	3.8×10^{-5} m/h (.34m/y)
Solids runoff rate from soil	U_{SW}	2.3×10^{-6} m/h (0.0002 m/y)
Water side MTC over sediment	k_{YW}	.01 m/h
Diffusion path length in sediment	Y_4	.005 m
Sediment deposition rate	U_{DX}	4.5×10^{-8} $m^3/m^2.h$ (.0004 m/y)
Sediment resuspension rate	U_{RX}	1.1×10^{-8} $m^3/m^2.h$ (.0001 m/y)
Sediment burial rate	U_{BX}	3.4×10^{-8} $m^3/m^2.h$ (.0003 m/y)
Leaching rate from soil to ground water	U_L	3.9×10^{-5} $m^3/m^2.h$ (.34 m/y)

Table 4

Calculation of D Parameters

Compartment	Process	Individual D	Total D
air(1) - water(2)	diffusion	$D_V = 1/(1/k_{VA}A_{12}Z_{11} + 1/k_{WA}A_{12}Z_{22})$	
-	rain	$D_{QW} = Z_{22} \cdot G_{QW}$	$D_{12}=D_V+D_{QW}+D_{DW}+D_{PW}$
-	wet deposition	$D_{DW} = G_{DW} \cdot Q \cdot \phi_{13} \cdot Z_{13}$	$D_{21}=D_V$
-	dry deposition	$D_{PW} = G_{PW} \cdot \phi_{13} \cdot Z_{13}$	
air(1) - soil(3)	diffusion	$D_S = 1/(1/k_{SA}A_{13}Z_{11} + Y_3/(A_{13}(B A_3 Z_{11} + B W_3 Z_{22})))$	
-	rain	$D_{QS} = G_{QS} \cdot Z_{22}$	$D_{13}=D_S+D_{QS}+D_{DS}+D_{PS}$
-	wet deposition	$D_{DS} = G_{DS} \cdot Q \cdot \phi_{13} Z_{13}$	$D_{31}=D_S$
-	dry deposition	$D_{PS} = G_{PS} \cdot \phi_{13} \cdot Z_{13}$	
soil(3) - water(2)			
-	soil runoff	$D_{SW} = G_S \cdot Z_{33}$	$D_{32}=D_{SW}+D_{WW}$
-	water runoff	$D_{WW} = G_W \cdot Z_{22}$	$D_{23}=0$
sediment(4)-water(2)	diffusion	$D_Y = 1/(1/k_{YW}A_{24}Z_{22} + Y_4/BW_4A_{24}Z_{22})$	
-	deposition	$D_{DX} = G_{DX} \cdot Z_{23}$	$D_{24}=D_Y+D_{DX}$
-	resuspension	$D_{RX} = G_{RX} \cdot Z_{43}$	$D_{42}=D_Y+D_{RX}$
reaction	either bulk phase	$D_{Ri} = k_{Ri}V_iZ_i$	$k_{Ri}V_iZ_i$
	or pure phase	$D_{Rij} = k_{Rij} \cdot V_{ij}Z_{ij}$	$\sum(k_{Rij}V_{ij}Z_{ij})$
advection	bulk phase	$D_{Ai} = G_iZ_i$	G_iZ_i

previously to account for a larger average chemical molecular weight and to correspond more closely to values reported for lakes.

The non-diffusive processes of chemical transfer by rain dissolution and wet and dry atmosphere deposition to water are described by the appropriate G_1Z_1 products as D_{QW} , D_{DW} , and D_{PW} , respectively. The method of calculating of these D values is given in detail by Mackay et al (3). Briefly, rain which falls at a rate U_Q of 9.7×10^{-5} ($m^3 \text{rain}/m^2 \text{area.h}$) or m/h or 0.85 m/year on water contains dissolved chemical in equilibrium with the air and with a concentration of C_Q mol/m^3 . The flux from air to water in the dissolved phase N_{QW} is expressed as

$$\begin{aligned} N_{QW} &= U_Q A_{12} C_Q = G_{QW} \cdot C_Q \\ &= D_{QW} \cdot f_1 \text{ (mol/h)} \end{aligned}$$

where G_{QW} is the volumetric flow rate of rain to the water surface (m^3/h). D_{QW} is thus $G_{QW} \cdot Z_{22}$, since C_Q is $Z_{22} f_1$.

For wet particulate deposition, each rain drop is considered to scavenge all particles from an atmospheric volume Q (200,000) times larger than itself. Since the particles occupy a volume fraction ϕ_{13} , the volumetric flux on water of chemical in association with wet particles, N_{DW} becomes

$$\begin{aligned} N_{DW} &= U_Q \cdot Q \cdot \phi_{13} \cdot A_{12} \cdot C_P \\ &= G_{DW} \cdot C_P \\ &= D_{DW} \cdot f_1 \end{aligned}$$

where D_{DW} is $G_{DW} \cdot Z_{13}$, G_{DW} is the wet deposition rate of particles on the water (m^3/h), and C_p is the chemical concentration on the particles.

For dry deposition of particles on water the flux is

$$\begin{aligned} N_{PW} &= U_p \cdot \phi_{13} \cdot A_{12} \cdot C_p \\ &= G_{PW} \cdot Z_{13} f_1 \\ &= D_{PW} \cdot f_1 \end{aligned}$$

Where G_{PW} (m^3/h) is the product of U_p , the dry particle deposition velocity (assumed to be 10.8 m/h or 0.003 m/s), the particle volume fraction, and the water area.

The transfer parameters necessary to calculate the net flux between bulk air and water become:

$$\text{air-water } D_{12} = D_v + D_{QW} + D_{DW} + D_{PW}$$

$$\text{water-air } D_{21} = D_v$$

$$\text{with total flux } N_{12} = D_{12}f_1 - D_{21}f_2$$

ii) Air-Soil

The bulk soil is viewed as a matrix 10 cm deep of air, water, organic and mineral matter. Diffusion from soils can take place in the air or water phases or in parallel in both and is usually described by Fick's first law as

$$\text{Flux} = AB \Delta C / \Delta x \text{ mol/l.}$$

where B is an effective diffusivity in air (B_{A1}) or water (B_{W1}) (m^2/h), ΔC is the concentration difference (mol/m^3) and ΔY is the diffusion path length (m) to which the difference applies. B is calculated as in the model developed by Jury et al. (8) using the Millington and Quirk expressions and the appropriate molecular diffusivity and phase volume fraction. For soil air, the effective diffusivity is

$$B_{A3} = B_{MA} \cdot \phi_{31}^{3.33} / (1 - \phi_{33})^2$$

where B_{MA} is air molecular diffusivity, ϕ_{31} is volume fraction of soil air and $(1 - \phi_{33})$ is the porosity of the soil.

Similarly, for diffusion in soil water (which is important for soluble, low volatility chemicals), the effective diffusivity is

$$B_{W3} = B_{MW} \cdot \phi_{32}^{3.33} / (1 - \phi_{33})^2$$

The D values for the parallel diffusive flows in soil air and water are

$$D_{AD} = B_{A3} \cdot A_{13} \cdot Z_{11} / Y_3 \quad \text{air}$$

$$D_{WD} = B_{W3} \cdot A_{13} \cdot Z_{22} / Y_3 \quad \text{water}$$

B_{A3}/Y_3 and B_{W3}/Y_3 can be considered equivalent to mass transfer coefficients in soil air and water, Y_3 being the soil diffusion depth of 5 cm or half the total depth.

In the interests of simplicity, common molecular diffusivities are used for all chemicals of 0.04 in air and 4×10^{-6} (m^2/h) in water.

A mass transfer coefficient k_{SA} (of 1 m/h) combined with the air fugacity capacity and area characterises the air-side diffusion parameter and

$$D_{SA} = k_{SA} A_{13} Z_{11}$$

Recalling that the resistance $1/D_{SA}$ is in series with the two parallel resistances, $1/D_{AD}$ and $1/D_{WD}$, total D for soil-air diffusion becomes

$$D_S = 1/(1/D_{SA} + 1/(D_{AD} + D_{WD}))$$

Non-diffusive transfer of chemical by atmospheric deposition is included to give total D values of

$$\text{air-soil } D_{13} = D_S + D_{DS} + D_{PS} + D_{QS}$$

$$\text{soil-air } D_{31} = D_S$$

where D_{DS} , D_{PS} , and D_{QS} are parameters for wet and dry deposition and rain wash out from air to soil and are calculated as for the air-water exchange but adjusted to reflect the soil-air interfacial area.

iv) Water-Sediment

Water-sediment diffusion is calculated similarly to soil-air diffusion. The effective diffusivity in sediment pore water is given by

$$\begin{aligned} B_{W4} &= B_{MW} \cdot \phi_{42}^{3.33} / (1 - \phi_{43})^2 \\ &= B_{MW} \cdot \phi_{42}^{1.33} \end{aligned}$$

and diffusion in pore water is represented by

$$D_{XW} = B_{W4} \cdot A_{24} \cdot Z_{22} / Y_4$$

where Y_4 the effective depth is 5 mm.

The total diffusive transport coefficient, D_Y , between sediment and water is

$$D_Y = 1 / (1/D_{XW} + 1/D_{YW})$$

where diffusion in the water boundary layer is described by the parameter

$$D_{YW} = K_{YW} \cdot A_{24} \cdot Z_{22}$$

and K_{YW} is the water-side mass transfer coefficient with a value of .01 m/h.

The one way processes of transfer by suspended sediment deposition and resuspension are described by "velocities" U_{DX} (4.5×10^{-8}) and U_{RX} (1.1×10^{-8}) m^3 solids/ m^2 area.h or m/h which are combined with sediment area to give flow rates G_{DX} and G_{RX} . The respective transfer parameters become

$$D_{DX} = G_{DX} \cdot Z_{23}$$

$$D_{RX} = G_{RX} \cdot Z_{43}$$

Inclusion of these parameters gives overall D values for sediment-water transfer

$$\text{water-sediment} \quad D_{24} = D_Y + D_{DX}$$

$$\text{sediment-water} \quad D_{42} = D_Y + D_{RX}$$

The sediment depth has been reduced to 10 mm which combines with a burial rate of $.0003 \text{ m}^3/\text{m}^2 \text{ y}$ of solids or 1 mm/year of sediment of porosity 0.7 to give a characteristic burial time of 10 years, which is reasonable for freshwater lakes.

v) Soil-Water

Transfer of chemical from soil to water is considered to take place in one direction only and includes transfer by water run-off, D_{WW} , and associated soil loss D_{SW} calculated from appropriate GZ values, ie

$$D_{WW} = G_W \cdot Z_{22}$$

$$D_{SW} = G_S \cdot Z_{33}$$

The parameters for total transfer become

$$\text{soil-water } D_{32} = D_{WW} + D_{SW}$$

$$\text{water-soil } D_{23} = 0$$

The water and solids run off rates from soil are expressed per unit area of soil and represent fairly heavy run off conditions. The solids runoff rate of .00023 m/y is chosen to balance the sediment burial rate of .0003 m/y, and the water runoff is assumed to be 40% of the rain rate of 0.85 m/y. These values are typical of precipitation and soil run-off rates reported by Environment Canada and the U.S. EPA for the Great Lakes Basin (9).

Reaction Parameters

As stated previously, reactive and advective processes are characterized by the parameters D_R and D_A with units of mol/Pa.h.

The model permits reaction in either the bulk or pure phase of each media but not in both simultaneously. The reaction rate constant is combined with the appropriate V and Z values. For example, for reaction in bulk air

$$D_{R1} = k_{R1}V_1Z_1$$

or for reaction in air particles

$$D_{R10} = k_{R10}V_{10}Z_{10}$$

If reaction occurs in more than one pure phase, the D values are summed to give a total for the bulk phases, that is

$$D_{RT1} = \sum k_{R1j} V_{1j} Z_{1j}$$

Advection Parameters

Advection is into and out of the bulk phases of air and water. However, it is possible to incorporate an advective flow in particulate matter. Inflow rates and residence times for air and water are given in Table 5.

Transfer to an altitude greater than 2 km, leaching from soil and sediment burial are included as advective processes. Transfer to higher altitude takes place at approximately 90 m/y (or .01 m/h), as discussed previously (3). The leaching rate from soil, which has been included in an attempt to detect chemicals which are potential groundwater contaminants, is set at 40% of the rain rate of 0.85 m/y. Sediment burial is assumed to take place at 0.3 mm/year and is equal to the difference between suspended sediment deposition and resuspension rates. The velocities are included in Table 3 and the residence times in Table 5.

We emphasize that these values have been selected largely on the basis of being typical of the Southern Ontario-Great Lakes region. They can easily be modified for other regions.

The only differences between the regional and evaluative models are the volumes, areas, and advective flow rates. Since all other rates are expressed on a unit area or volume basis, they apply to both models.

Table 5

Advection Rates and Residence Times

		Volume (m ³)	Flow Rate (m ³ /h)	Residence Time (h)
Air	S. Ontario	4x10 ¹⁴	3.3x10 ¹²	120
	Evaluative	2x10 ⁹	1.7x10 ⁷	120
Water	S. Ontario	4x10 ¹²	3.3x10 ⁸	12000 (500 days)
	Evaluative	2x10 ⁷	1700	12000 (500 days)
	Transfer to		2.1x10 ⁹	22 years
	higher altitude	Evaluative	1x10 ⁴	22 years
Leaching from soil	S. Ontario		4.66x10 ⁶	
	Evaluative		23.3	
Sediment burial	S. Ontario		2740	10 years
	Evaluative		0.014	10 years

Emissions

Emissions N_{Ei} (mol/h) may be into any or all of the bulk phases.

Mass Balance Equations

Mass balance equations are set up for the four bulk phases which incorporate emissions, transfer between adjacent phases, and degradative and advective flows. The equations take the form:

$$N_{E1} + D_{A1}f_{B1} = \sum_j [f_1 D_{1j} - f_j D_{j1}] + D_{A1}f_1 + D_{R1}f_1$$

$$\text{or } N_{E1} + D_{A1}f_{B1} - f_1[\sum_j D_{1j} + D_{A1} + D_{R1}] + \sum_j [D_{j1}f_j] = 0$$

The solution is algebraic as shown in Figure 1. From the bulk phase fugacities, the concentrations and amounts for all phases are calculated as well as transfer and reaction rates.

Figure 1. Algebraic Solution of Model Equations

$$f_2 = X_1 / Y_1$$

$$f_1 = J_1 + K_1 f_2$$

$$f_3 = J_3 + J_1 K_3 + K_1 K_3 f_2$$

$$f_4 = J_4 + K_4 f_2$$

where $I_1 = D_{12} + D_{13} + D_{A1} + D_{R1} + D_{ST}$

$$I_2 = D_{21} + D_{24} + D_{A2} + D_{R2}$$

$$I_3 = D_{31} + D_{32} + D_{R3} + D_L$$

$$I_4 = D_{42} + D_{R4} + D_{BX}$$

$$J_1 = [NET_1 + D_{31} J_3] / [I_1 - D_{31} K_3] \quad K_1 = D_{21} / [I_1 - D_{31} K_3]$$

$$J_3 = NE_3 / I_3$$

$$K_3 = D_{13} / I_3$$

$$J_4 = NE_4 / I_4$$

$$K_4 = D_{24} / I_4$$

$$X_1 = NET_2 + J_1 D_{12} + [J_3 + J_1 K_3] D_{32} + J_4 D_{42}$$

$$Y_1 = I_2 - K_1 D_{12} - K_1 K_3 D_{32} - K_4 D_{42}$$

$$NET_1 = NE_1 + D_{A1} f_{B1}$$

$$NET_2 = NE_2 + D_{A2} f_{B2}$$

MODEL OUTPUT

The regional and evaluative model outputs include the input chemical properties, the dimensions and properties of all bulk and subcompartments, input reaction rate constants, input emission rates, and any background (advective inflow) concentrations. All fugacities are provided, as are concentrations, in mol/m^3 and conventional units. Transfer rates and D values are given for individual and combined processes. A total mass balance can be assembled, as shown for PCBs in Figure 2, from which the overall chemical persistence is calculated.

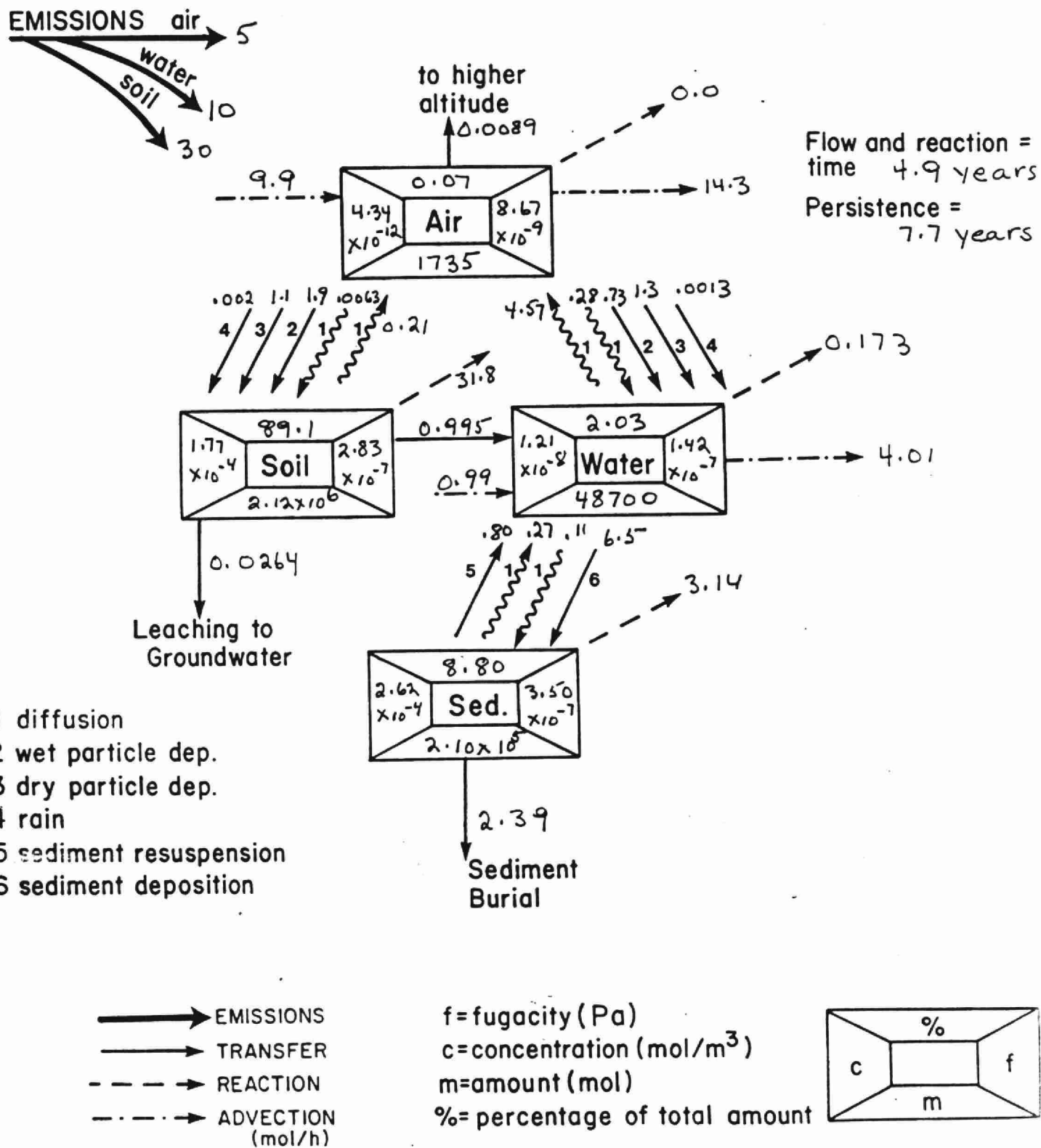


Figure 2. Mass Balance for PCBs in the Great Lakes

DISCUSSION

Models such as this cannot be "validated" in the same sense that a simpler physical or chemical model can be validated. Environmental concentrations vary in time and space, and few data are usually available. Reaction rate constants vary diurnally and seasonally. Emissions are rarely known accurately. There are variations and uncertainties in transport rate parameters, such as deposition and resuspension rates. Few environments are at steady state as described here. The best that can be hoped for is that the model corresponds with order of magnitude fidelity to fragmented observations for a variety of chemicals of quite different properties and pathways. The chemical-to-chemical variation should be described entirely by the chemicals' properties and emission rates and not by adjustable parameters describing environmental processes. But even this modest model capability is invaluable for predicting the behavior of new chemicals and for estimating order of magnitude concentrations.

As part of the model development, the model was run for selected chemicals of varying properties, environmental concentrations were calculated, and compared with observations. A common problem is estimation of emission rates. In some cases, it is necessary to back-calculate what the emissions may be or must be to create prevailing concentrations, then check if these emission rates are in reasonable accord with rates of production or use.

The chemicals selected and their properties are listed in Table 6. Emissions, background inflow concentrations, and degradation rate constants are listed in Table 7. In the case of benzene, benzo(a)pyrene (BAP), and 2,3,7,8 TCDD, production data were used to estimate emissions. In the case

Table 6. Physical Chemical Properties of Selected Chemicals

Compound	mol. wt. (g/mol)	V.P. (Pa)	Sol'y (g/m ³)	log K _{ow}
6-DB (10)	350	5.0e-04	3.5e-03	6.8
benzene	78.11 (11)	1.27e04 (12)	1.78e03 (12)	2.13 (13)
benzo(a)pyrene	252.3 (11)	7.3e-07 (11)	3.8e-03 (13)	5.98 (13)
HCB	284.8 (11)	1.5e-03 (12)	5.0e-03 (13)	5.47 (13)
airax	545.59 (11)	1.3e-04 (14)	.00007 (14)	6.89 (3)
2,3,7,8 TCDD (15)	322	.0002	1.93e-05	6.8
TCE	131.5 (11)	9.87e03 (3)	1.1e03 (3)	2.29 (3)

Table 7. Emissions, Background Inflow Concentrations and Degradation Rate Constants of the Chemicals

compound	Emissions (mol/h)			Inflow concn (mol/m ³)		Degradation rate constants (h ⁻¹)				
	air	water	soil	air	water	air	water	soil	sediment	fish
p-CE	5 (f)	10 (f)	30 (f)	3e-12 (e)	3e-09 (e)	-	1.5e-05 (e)	1.5e-05 (e)	1.5e-05 (e)	1e-06 (e)
benzene	1e04 (16)	8e04 (16)	-	3e-08 (e)	-	8.6e-04 (3)	4.76e-03 (3)	-	-	-
benzo(a)pyrene	50 (17,18)	1 (17,18)	50	2e-11 (e)	-	-	3.5e-05 (18)	3.5e-05 (18)	-	-
HCB	1 (f)	8 (f)	1 (f)	-	-	1.44e-02 (3)	-	1.9e-05 (3)	-	-
mirex	-	.004 (19)	-	-	-	-	1.93e-04 (3)	-	-	-
2,3,7,8 TCDF	.01 (20)	.001 (e)	.001 (e)	3e-15 (e)	1e-11	.01	8e-02 (20)	1.1e-05 (20)	9.3e-05 (21)	-
TCE	6.2e05 (22)	6.0e03 (e)	-	1.98e03(22)	-	.01 (22)	1.0e-04 (22)	-	-	-

of 6-CB, hexachlorobiphenyl (HCB), and mirex, emissions were estimated on the basis of known uses and disposal methods. Rate constants were taken from the literature and judgement was used to select a value where a range of data existed.

Table 8 lists the calculated bulk compartment concentrations and gives reported values for comparison. Table 9 summarises the predicted phase concentrations and fugacities.

PCBs

For PCBs (specifically represented in this case by a hexa-chloro-biphenyl), the primary sources are water advection inflow (mainly the Niagara River) of 1 ng/L and air advection at 1 ng/m³, but with additional local emissions into soil and water due to transformer leakage, waste disposal, and seepage from landfill with a small amount being released to the atmosphere through combustion.

The conditions shown are believed to represent those prevailing in the Southern Ontario region in the mid-1980s. Much higher concentrations were believed to have been experienced in the early 1970s. For example, gull egg concentrations were then about a factor of ten higher than current values.

The dominant fate processes are atmospheric deposition, volatilization, and sediment deposition. Reported concentrations of total PCBs are in good agreement (ie., within a factor of five) with model estimates, but it should be noted that it is possible to adjust emission rates to improve the

Table 8. Comparison of Calculated and Reported Concentrations for the Four Bulk Phases and Fish

Compound	Air (ng/m ³)		Water (ng/L)		Soil (ng/kg)		Sediment (ng/g)		Fish (ng/kg)	
	predicted	reported	predicted	reported	predicted	reported	predicted	reported	predicted	reported
6-CB	1.5	1-10 (23)	4	1-10 (23)	.04	.01-.02 (23)	65	10-100 (23)	.4	N.D.-1.7 (23)
benzene	2000	16000 (24) (N.D.-2.8e05)	290	<10000 (24)	.0001	-	0.5	-	.002	-
benzo(a)pyrene	1.6	1.32 (24) 7.1 (17) 4.7 (18)	6.4	28.2 (18)	.03	.1 (24) .1 (17) .3-.5 (18)	110	80-300 (24)	.15	.14 (24)
HCB	.2	.2 (24)	2.7	.05-1 (24)	.0009	-	25	3-100 (24)	.01	.05 (25) .003 (26)
dioxin	.0001	-	.002	.002 (27) 30 (24) <1 (28)	8e-06	-	.07	20 (24) 69 (29)	.0001	.003 (25) N.D.-.04 (24)
2,3,7,8 TCDD	.0001	.0001 (29)	3.5e-05	-	2e-06	<3e-06 (20)	0.0002	0.0003 (30)	1e-06	1e-06 (20)
TCE	11000	6400 (22)	270	<6000 (22)	3.7e-05	-	0.6	.07 (22)	0.0026	0.0001-0.01 (22)

Table 9. Fugacities f (Pa) and concentrations C (mol/m³) for the 7 chemicals

Chemical		6-CB		Benzene		BAP		HCB		Mirex		TCDD		TCE	
		f	C	f	C	f	C	f	C	f	C	f	C	f	C
Air	bulk	8.67E-09	4.34E-12	7.97E-05	3.21E-09	9.65E-11	6.44E-12	1.89E-09	8.21E-13	2.53E-13	1.96E-16	5.83E-12	3.76E-15	2.13E-04	8.58E-08
	pure		3.50E-12		3.21E-08		3.89E-14		7.60E-13		1.02E-16		2.35E-15		8.58E-08
	particles		4.20E-02		1.52E-05		3.20E-01		3.04E-03		4.71E-06		7.06E-05		5.22E-05
Water	bulk	1.42E-07	1.22E-08	2.07E-03	3.71E-06	6.22E-10	2.55E-08	2.94E-07	4.49E-09	4.33E-10	3.86E-12	1.09E-11	2.45E-14	2.46E-03	2.09E-06
	pure		2.85E-09		3.71E-06		1.28E-09		3.44E-09		4.28E-13		3.25E-15		2.09E-06
	particles		1.78E-03		9.87E-05		2.42E-03		2.00E-04		6.55E-07		4.05E-09		8.02E-05
	biota		4.32E-04		2.40E-05		5.88E-04		4.87E-05		1.59E-07		9.85E-10		1.95E-05
Soil	bulk	2.83E-07	1.77E-04	8.01E-05	2.41E-07	8.83E-10	1.72E-04	1.39E-07	4.74E-06	2.99E-10	2.26E-08	1.46E-09	2.73E-08	2.13E-04	4.19E-07
	air		1.14E-10		3.23E-08		3.56E-13		5.61E-11		1.21E-13		5.91E-13		8.60E-08
	water		5.67E-09		1.44E-07		1.82E-08		1.63E-09		2.95E-13		4.39E-13		1.81E-07
	particles		3.54E-04		3.83E-07		3.43E-04		9.47E-06		4.52E-08		5.46E-08		6.95E-07
Sediment	bulk	3.50E-07	2.62E-04	2.07E-03	8.53E-06	2.57E-09	6.00E-04	9.15E-07	3.74E-05	2.11E-09	1.91E-07	3.86E-12	9.64E-11	2.47E-03	6.29E-06
	water		7.00E-09		3.71E-06		5.30E-08		1.07E-08		2.08E-12		1.16E-15		2.09E-06
	particles		8.73E-04		1.98E-05		2.00E-03		1.25E-04		6.38E-07		2.88E-10		1.61E-05

"fit". PCBs are a very convenient calibrating chemical for models because they migrate widely throughout the environment and are well-studied.

Benzene

Production of benzene as a chemical and fuel in Southern Ontario is reported to be approximately 6×10^9 kg/year. It is assumed that its use as an industrial chemical and fuel results in a 1% loss to the environment, of which 90% is probably into water due to waste disposal and 10% into air due to fuel combustion and evaporation. An advective flow in air of 2 ug/m^3 was assumed.

Predicted values for air and water concentrations are low by a factor of 10. There are no reported data for soil and sediment, due probably to its low concentrations caused by its short estimated half-life of 5 days.

It is probable that the low concentration reflects the prevalence of measurements in urban areas where there is a much higher than average fuel use. A good match of model estimates with observations is obtained if it is assumed that emissions are a factor of ten higher. This could represent emission of say 90% of the benzene in 10% of the region's area. The estimated sediment, soil, and fish concentrations are very low, thus it is unlikely that monitoring these compartments will be useful.

Benzo(a)pyrene

Benzo(a)pyrene (BAP) is mainly an atmospheric pollutant which is deposited in association with particulate matter, resulting in widespread contamination of soil and sediments. The emissions of 65% into air and 35% into soil assume additional direct soil contamination from aviation and automotive fuels. An air advective inflow concentration of 1 ng/m^3 is based on data reported by Canviro (17). BAP has been the subject of modelling by Ryan and Cohen (18).

As with benzene, it is likely that regions in which there is a higher than average fuel usage, especially diesel fuel usage, experience concentrations which are larger by a factor of ten than those estimated by the model.

Hexachlorobenzene

The main route of entry of hexachlorobenzene (HCB) into the environment is in waste water streams, soil application of pesticides, and spillage. It is highly hydrophobic and sorbs strongly to suspended sediments with subsequent deposition to sediment. It is bioconcentrated by fish.

Emissions are assumed to be 80% into the water and 10% each into soil and air. This results in a relative distribution that is in agreement with reported concentrations. The absolute value of the emissions were chosen to produce levels of the correct order of magnitude. It is not known if these emissions are correct.

Mirex

Mirex has been used as a pesticide and a flame retardant. Its main routes of entry to the Great Lakes have been via the Niagara and Oswego Rivers from production plants in the U.S. It has been extensively monitored in Lake Ontario. Sediment and suspended sediment concentrations are well quantified, but water concentrations are now generally below 1 ng/L. Measurements have been made by Yin (25) of 2 pg/L. Warry and Chan (19) estimated loadings of 13-20 kg per year to Lake Ontario in association with suspended matter. Good agreement was found between predicted and reported water concentrations for these emissions. Sediment concentrations are underpredicted, which is probably due to previous contamination.

Mirex is interesting because it represents a situation in which there was a high emission rate in the past, but present emissions are small. If the model is run for two emission scenarios corresponding to concentrations of inflow water differing by a factor of 500, then good agreement is obtained with concentrations experienced in the 1970s and with prevailing concentrations. The steady-state model can thus be used to estimate unsteady state behaviour, provided that account is taken of the response time of the system, which in this case is 12.5 years.

2,3,7,8 Tetrachloro Dibenzo-p-Dioxin (TCDD)

Polychlorinated dibenzo-p-dioxins form a group of 75 congeners which enter the environment as by-products of combustion, waste disposal, and pesticide manufacture. They are variable in toxicity, with 2,3,7,8 TCDD being the most toxic. Direct measurements of 2,3,7,8 TCDD are not available, but it is estimated that approximately 40 kg/year enter the Ontario region as 2,3,7,8 TCDD "toxic equivalents" (20). It is assumed that 80% of this amount is into the air and 10% each into soil and water. It is included here primarily to illustrate the applicability of the model to "new" chemicals. Atmospheric transport and deposition in association with particulate matter are the dominant processes. The agreement between estimated and the few reported concentrations is good.

Trichloroethylene (TCE)

TCE, a major industrial solvent, is introduced mainly into the air due to its high vapor pressure. A small percentage (estimated here as 1%) is introduced to the aquatic environment through wastewater and disposal.

The Ontario emissions are scaled from U.S. production data (22). A background atmospheric inflow of 80 ng/m³ is included.

The resulting concentrations are in excellent agreement with data from La Jolla, California, and Liverpool, England, as well as the model predictions of Cohen and Ryan (22).

DISCUSSION

The model provides a relatively simple, rapid method of establishing the relative importance of environmental fate processes for specific chemicals using a minimum of input data. It is believed to give an adequate characterization of the dominant phases of accumulation. For example, mirex is 62% in soil and 35% in sediments, while benzene is 46% in air and 53% in water. These percentages are controlled by the emission sources and the chemicals' properties. An overall persistence or residence time is also estimated which ranges from 6 days for benzene to 12 years for mirex. This persistence is a function of partitioning, reaction rates, and advection rates. The relative importance of advective inflow and local emissions can be estimated.

The evaluative 1 sq km version can be used to determine the dominant environmental partitioning pathways and the persistence of a chemical, using illustrative rather than real emissions. The computed absolute concentrations have no significance. Since many jurisdictions have interest in estimating the environmental fate of chemicals and the regions corresponding to these jurisdictions have differing ratios and natures of air, water, soil, and sediments, it is useful to have a common evaluative test system which can be used by various jurisdictions to inter-calibrate environmental assessments. The combination of evaluative and region-specific environments thus provides a convenient system for international assessment of chemicals.

A useful feature of both models is that a sensitivity analysis is possible by which the effects of varying properties of the chemicals and the environment can be explored. This establishes which properties should be estimated most accurately and can provide an estimate of likely error in concentration as a function of error in property.

If emission estimates are available, the model can be used to estimate concentrations with, it is believed, order of magnitude (factor of 10) accuracy. It is most reliable for substances, such as PCBs, which are persistent and widely dispersed in the environment. The model can be used as an interpretive tool to explore temporal and spatial variations in concentrations. For example, it appears that mirex has been discharged at two time periods at emission rates which have differed by a factor of approximately 500. Since the model is linear, concentrations are linearly related to emissions, thus there is no need to run the model repeatedly to explore such changes. Certain contaminants, such as benzene and BAP are emitted with considerable spatial variation. It can, therefore, be misleading to use average emissions and concentrations. It should be possible to develop "rules", which may be region-specific, that one would expect to encounter local concentrations which are perhaps a factor of 10 or 20 higher than average.

These concentrations could be of value in three respects. First, they provide guidance about likely prevailing environmental concentrations in the various media which result from present or possible future emissions. This is useful in designing analytical monitoring and identification programs.

Second, they provide guidance as to the proximity of the concentrations to those which are judged to be of toxicological or aesthetic significance. Generally, the estimated concentrations will be (or should be) well below lethal concentrations, but the quotient of effect-to-estimated concentration provides a numerical expression of the "safety factor". Chemicals with low quotients are presumably of greatest concern and thus require priority treatment. The combination of the model with toxicological concentration information thus provides a method of establishing priorities among the large number of chemicals in present use and helps to establish the relative priority of new chemicals.

Third, the concentrations provide a starting point for estimation of human exposure. Air inhalation and water ingestion rates can be combined with the appropriate media concentrations to estimate exposure by these routes. The relative importance of these routes then becomes obvious.

The importance of plants and vegetation as a source of human and animal intake of contaminants is now widely recognized. Persistent organic compounds, such as pesticides, herbicides, PCBs, and dioxins, have been found to partition into grains (31), fruits and vegetables (26, 32), pine needles (33), and moss and lichens (34). They thus become directly available to herbivores and humans through the ingestion of grains, fruits and vegetables, and indirectly through the consumption of domestic animals and milk.

Attempts are being made, notably by Travis and co-workers (35), to relate concentrations in plants and animals to those of soil and air, as estimated from models such as this. Estimates can then be made of human intake by ingestion of these foods in appropriate "market-basket" ratios. Intake by fish consumption can also be included.

The exposure assessment can be extended further to include a recently developed steady-state physiologically based pharmacokinetic model (36) to predict partitioning, accumulation, and persistence in various animal or human tissues after prolonged, continuous exposure. Human tissue concentration data is usually not available for direct validation, but extrapolation from animal to human models is possible. Calabrese (37) has discussed the relevance of physiologically-based pharmacokinetic animal models for human risk assessment of cancer through exposure to chemical carcinogens. Although interspecies and intraspecies variation in susceptibility and heterogeneity of human response to toxic agents are areas of concern, the models can be used to quantify target organ doses between species.

Ultimately, it is believed, a capability will emerge to combine environmental, human exposure, and pharmacokinetic models in an overall process of tracking the pathways of a chemical including its sources, its distribution in various environmental media, such as air, water, soil, sediment, and food (as estimated here), its availability or exposure to animals and humans, and finally, to physiological target tissues.

Finally, we believe that the model can be, and should be, improved by obtaining better estimates of certain transport and partitioning parameters. For example, the mass transfer coefficients and diffusivities are average values applied to all chemicals. Chemical specific and region specific values could be used instead to measure accuracy. Most important, the model should be tested more thoroughly against a variety of chemicals of widely differing properties. The principal difficulties in accomplishing this are the lack of emission data, environmental concentration data, reaction rate constants and physical chemical properties.

CONCLUSIONS

A regional fugacity model has been developed, tested with six chemicals, and found to give a reasonable picture of environmental partitioning, reaction, advection, and transport characteristics. Estimated concentrations are in order-of-magnitude accord with reported values, but there are considerable uncertainties in the emission rates on which these concentrations depend. The estimated concentrations may be of value for designing analysis programs, for setting priorities, and for assessing human exposure to present and new chemicals.

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